

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 909 582 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
21.04.1999 Bulletin 1999/16

(51) Int Cl. 6: B01J 29/06, C10G 11/05,
B01J 29/40, B01J 29/46

(21) Application number: 98308445.0

(22) Date of filing: 15.10.1998

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 15.10.1997 CN 97119012

(71) Applicants:
• CHINA PETROCHEMICAL CORPORATION
Beijing (CN)
• RESEARCH INSTITUTE OF PETROLEUM
PROCESSING, SINOPEC
Beijing (CN)

(72) Inventors:
• Shi, Zhicheng,
Research Inst. of Petrole. Process.
Haidian District, Beijing (CN)

• Zhang, Fengmei,
Research Inst. of Petrol. Process.
Haidian District, Beijing (CN)
• Liu, Shunhua,
Research Inst. of Petroleu. Process.
Haidian District, Beijing (CN)

(74) Representative: Colmer, Stephen Gary et al
Mathys & Squire
100 Gray's Inn Road
London WC1X 8AL (GB)

Remarks:

A request for correction in the description has been filed pursuant to Rule 88 EPC. A decision on the request will be taken during the proceedings before the Examining Division (Guidelines for Examination in the EPO, A-V, 3.).

(54) Cracking catalytic for the production of light olefins and its preparation

(57) A catalyst for catalytic cracking process for the production of light olefins comprises 10~70wt% (based on the weight of catalyst) of clay, 5~85wt% of inorganic oxides and 1~50wt% zeolite, wherein said zeolite is a mixture of 0~25wt% of Y type zeolite and 75~100wt% of phosphorus and aluminum or phosphorus and magnesium or phosphorus and calcium containing high silica zeolite having a structure of pentasil; said pentasil high silica zeolite being one selected from the group

consisting of ZSM-5, ZSM-8 and ZSM-11 of zeolites containing 2~8wt% of phosphorus and 0.3~3wt% of aluminum or magnesium or calcium (calculated as the oxides), having a silica/alumina mole ratio of 15-60. The catalyst exhibits excellent activity stability and high yields of light olefin, especially for ethylene, also method for preparation of the catalyst. It can attain the same level of yields of light olefins as that of steam thermal cracking at a lower reaction temperature than that of steam thermal cracking.

EP 0 909 582 A1

Description**Field of the Invention**

5 [0001] This present invention relates to a petroleum hydrocarbon catalytic pyrolysis catalyst for producing light olefins, and the process for preparing the same, and more particularly to a petroleum hydrocarbon catalytic pyrolysis catalyst for producing mainly ethylene, propylene, and also butylene as by-products.

Background of the Invention

10 [0002] The traditional method for the production of ethylene from petroleum hydrocarbon is by steam thermal cracking in tubular furnace. The feeds adopted in steam thermal cracking are ethane, propane, butane, naphtha or atmospheric gas oil (AGO). The method using heavier hydrocarbon thermal cracking on solid heat carrier for producing ethylene also exists. The heat carriers generally adopted are inert solid particles such as quartz sand, coke, coke carbon, etc.

15 [0003] Quite a few literatures reported the methods relating the production of light olefins by petroleum hydrocarbon cracking or pyrolysis conversion with catalysts. USP 3,541,179, USP 3,647,682, DD 225,135 and SU 1,214,726 adopt the oxides supported metal catalysts, wherein the support can be $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ or other oxides and the metal components are selected from elements of IIB, VB, VIIB and VIIIB groups. As the supported metal possesses dehydrogenation property, it also accelerates the condensation and coking reaction during the reaction process of cracking. Hence, this type of catalysts can only be used for processing light feed stocks ($< 220^\circ\text{C}$). Some patents adopt the composite oxides as catalysts, for example, USP 3,725,495 and USP 3,839,485 reported the catalysts comprising mainly ZrO_2 and/or HfO_2 , and also Al_2O_3 , Cr_2O_3 , MnO_2 and/or Fe_2O_3 and alkali and alkaline metal oxides. Although alkali and alkaline earth metal oxide catalysts can promote the yield of ethylene, quite a lot of CO and CO_2 will be formed simultaneously.

20 [0004] In the field of the production of light olefins by petroleum hydrocarbon cracking with solid acid catalyst, DD 152,356A adopts the amorphous $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ catalyst for cracking various liquid hydrocarbon and hydrocarbon fractions including gasoline, kerosene, gas oil or vacuum distillates, at $600\text{--}800^\circ\text{C}$ to produce light olefins with a $\text{C}_2\text{--}\text{C}_4$ olefin yield of 40~50wt% based on the feed. JP 60-224,428 disclosed a cracking catalyst using HZSM-5 as active component and alumina as matrix, for catalytic cracking a feed stock of $\text{C}_2\text{--}\text{C}_{25}$ paraffinic hydrocarbons at $600\text{--}750^\circ\text{C}$ to obtain a $\text{C}_2\text{--}\text{C}_4$ olefin yield of roughly 30wt%. USP 3,758,403 revealed that a catalyst comprising both ZSM-5 zeolites and a large pore zeolite (e.g. X type or Y type)-as active components in a ratio of 1:10~3:1 displayed a performance of raising gasoline octane number while increasing $\text{C}_3\text{--}\text{C}_4$ olefin yield to about 10wt%. In CN1069016A, a catalyst comprising 30~90wt% SiO_2 , 20~70wt% Al_2O_3 , 0.5~30wt% alkali and alkaline earth metal oxides and 1~30wt% faujasite can produce 17~27wt% yield of C_2 , 30~40wt% yield of $\text{C}_2\text{--}\text{C}_4$ at $650\text{--}900^\circ\text{C}$ with the heavy hydrocarbon as feedstock. In USP4,980,053, a catalyst comprising HZSM-5 as active component supported on kaolin matrix obtained 40wt% yield of $\text{C}_3\text{--}\text{C}_4$ by cracking the heavy hydrocarbon feed at $500\text{--}650^\circ\text{C}$, but the yield of C_2 was low. In CN1083092A, an acidic molecular sieve catalyst containing crosslinking pillared interlayered montmorillonite molecular sieve and/or rare earth pentasil high silica zeolite is used for cracking heavy hydrocarbons at 680~780 and obtains a yield of 23wt% C_2 and 50 wt% $\text{C}_2\text{--}\text{C}_4$. USP 5,380,690 and ZL CN93102783.7 revealed a catalyst using a Y type zeolite and a phosphorus and rare earth containing high silica zeolite having a structure of pentasil as active components, and this catalyst with heavy oil fractions as feed stock can increase at $500\text{--}600^\circ\text{C}$ the gasoline octane number as well as the yield of $\text{C}_2\text{--}\text{C}_4$, mainly the yield of C_3 and C_4 .

30 [0005] The object of the present invention is to provide a novel zeolite-containing catalyst, said catalyst can attain the same level of yield of light olefins as that of steam thermal cracking at a lower reaction temperature than that of steam thermal cracking.

35 [0006] Another object of the present invention is to provide a method for preparing the said catalyst.

40 [0007] The further objects including the application of the said catalyst can be all learned from the content of the specification of the present invention including the examples.

45 [0008] The present invention provides a catalyst comprising a phosphorus-aluminum, phosphorus-magnesium or phosphorus-calcium containing high silica zeolite having the structure of pentasil prepared. The phosphorus existing in the zeolite enables the zeolite to have higher hydrothermal activity-stability; aluminum or magnesium or calcium existing in the zeolite can adjust the acidity of the zeolite, which is favorable to the formation of C_2 . During the catalytic pyrolysis process in the presence of an acidic catalyst, hydrocarbon cracking reaction is carried out based on the carbonium ion reaction mechanism, hence the light olefins produced are mainly C_3 and C_4 . C_2 is commonly formed by free radical reaction mechanism in thermal cracking hydrocarbons, therefore acidic catalyst is unfavorable for the formation of C_2 . The acidity of the zeolite of the present invention is appropriately adjusted, thus the catalyst of the invention not only decreases the activation energy of the hydrocarbon cracking reaction, and consequently the reaction can proceed at a lower temperature than that of steam thermal cracking, but also increases the yield of C_2 .

[0009] The present invention provides a catalyst comprising 10~70wt% (based on the weight of the catalyst) of clay, 5~85wt% of inorganic oxides, and 1~50wt% of zeolite, said zeolite is a mixture of 0~25wt% of Y type zeolite and 75~100wt% phosphorus-aluminum, phosphorus-magnesium or phosphorus-calcium containing high silica zeolite having a structure of pentasil.

[0010] Said clay in the catalyst of the invention can be all kind of clays usually used as a carrier for cracking catalyst, either natural or synthesized such as kaolin and kaolin polyhydrate, and may optionally be subjected to various chemical and/or physical treatment.

[0011] Said inorganic oxides in the catalyst of the invention are selected from amorphous $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$, Al_2O_3 and/or SiO_2 .

[0012] Said Y type zeolite in the catalyst of the invention may be a rare earth metal ion exchanged Y (REY) zeolite with a content of rare earth not less than 14wt% (calculated as RE_2O_3), and may also be a stabilized high silica Y type zeolite with a higher silica/alumina mole ratio prepared by various chemical and/or physical method, such as hydrothermal method, acid treatment, framework silicon enriching method, or SiCl_4 treatment method.

[0013] Said phosphorus and aluminum or phosphorus and magnesium or phosphorus and calcium containing high silica zeolite having a structure of pentasil in the catalyst of the invention is a kind of high silica zeolite containing 2~8wt% (based on the weight of zeolite) of phosphorus (calculated as P_2O_5) and 0.3~3wt% of aluminum or magnesium or calcium (calculated as oxide), such as ZSM-5, ZSM-8 or ZSM-11 type zeolite, having a silica/alumina mole ratio of preferably 15~60. The said phosphorus and aluminum or phosphorus and magnesium or phosphorus and calcium containing high silica zeolite having a structure of pentasil may also contain 0.3~3wt% (based on the weight of zeolite) of nickel (calculated as oxide).

[0014] The preparation method of the catalyst of the invention is as follows: mixing the precursor of the inorganic oxides with clay according to a predetermined ratio, adding de-cationized water to obtain a slurry with a solid content of 10~50wt%, adjusting and maintaining the pH value of the slurry to 2~4 using an inorganic acid such as hydrochloric acid, nitric acid, phosphoric acid or sulfuric acid, after aging statically at 20~80°C for 0~2 hrs adding into it a pre-calculated amount of zeolite, homogenizing, spray drying, washing off the free sodium ions and drying.

[0015] Said precursor of the inorganic oxides is selected from aluminum sol, pseudo-boehmite, silica sol or its mixture, and silica-alumina sol or gel.

[0016] Said clay can be all kind of clays usually used as a carrier for cracking catalyst, either natural or synthesized, such as kaolin, kaolin polyhydrate, and may optionally be subjected to various chemical and/or physical treatment.

[0017] Said inorganic acids are selected from hydrochloric acid, nitric acid, phosphoric acid or sulfuric acid.

[0018] Said zeolite is a phosphorus and aluminum or phosphorus and magnesium or phosphorus and calcium containing high silica zeolite having a structure of pentasil or a mixture of said high silica zeolite and a Y type zeolite, wherein the former is a kind of high silica zeolite containing 2~8wt% (based on the weight of zeolite) of phosphorus (calculated as P_2O_5) and 0.3~3 wt% of aluminum or magnesium or calcium (calculated as oxide) such as ZSM-5, ZSM-8 or ZSM-11 type zeolite, having a silica/alumina mole ratio of preferably 15~60.

[0019] The said high silica zeolite may also contain 0.3~3% (based on the weight of zeolite) of nickel (calculated as oxide).

[0020] The preparation method of the said zeolite is as follows: mixing homogeneously the high silica zeolite having a structure of pentasil with an aqueous solution containing phosphorus and aluminum or phosphorus and magnesium or calcium compounds according to a water/solid weight ratio of 1~3:1, impregnating for 0.5~4 hrs, drying at 100~120°C, and then calcining at 450~650°C for 1~4 hrs. Nickel on the said high silica zeolite can also be introduced by mixing nickel compound together with phosphorus and aluminum or phosphorus and magnesium or phosphorus and calcium compounds in an aqueous solution and impregnating said high silica zeolite in said aqueous solution. The said high silica zeolites having a structure of pentasil are the type of high silica zeolites of ZSM-5, ZSM-8 or ZSM-11 type having a silica/alumina mole ratio of preferably 15~60. The said phosphorus compound containing aqueous solution is preferably the aqueous solution of phosphoric acid, the aluminum or magnesium or calcium compound containing aqueous solution can be the aqueous solution of the nitrate, hydrochloride and sulfate of these elements, preferably the aqueous solution of nitrate or hydrochloride. The said nickel compounds can be nitrate, hydrochloride, or sulfate.

[0021] The Y type zeolite in the catalyst of the invention can be the rare earth metal ion exchanged REY zeolite having a rare earth metal content of not less than 14wt% (calculated as RE_2O_3) based on the weight of the zeolite, and may also be a stabilized high silica Y type zeolite having a higher silica/alumina mole ratio prepared by various chemical method and/or physical method, such as hydrothermal method, acid treatment method, framework silicon enriching method, or SiCl_4 treatment method.

[0022] The catalyst provided by the present invention can attain the same level of yield of light olefins as that of steam thermal cracking reaction at a lower reaction temperature than that of steam thermal cracking reaction. The said catalyst displays the excellent hydrothermal activity-stability as well as the yields of light olefins, especially the yields of $\text{C}_2^=$ and $\text{C}_3^=$. For example, the said catalyst can achieve a yield of 20wt% (based on the feed) of $\text{C}_2^=$, with the total yields of $\text{C}_2^=$ ~ $\text{C}_4^=$ being up to 54wt% under the reaction conditions of 680°C, a catalyst/oil weight ratio of 10 and WHSV

(weight hour space velocity) of 10 hrs⁻¹, using VGO (vacuum gas oil) as feedstock.

[0023] The present invention will be further described with reference to the following examples, which, however, shall not be construed to limit the scope of the present invention.

[0024] The phosphorus and aluminum or phosphorus and magnesium or phosphorus and calcium containing high silica zeolite, which may optionally contain nickel, having a structure of pentasil used in the examples is prepared as follows: ion-exchanging the commercial product of ZSM-5 zeolite having a silica/alumina mole ratio of 25 with ammonium nitrate solution according to a weight ratio of zeolite (anhydrous basis) : ammonium nitrate : de-cationized water = 1:1:20 at 90°C for 2 hrs, after filtering and leaching the resultant was ion-exchanged once more to obtain ammonium type of ZSM-5 with the sodium content (calculated as Na₂O) of less than 0.15wt% based on the weight of the zeolite, mixing said homogeneously ammonium type of ZSM-5 with a H₃PO₄, de-cationized water and AlCl₃ or MgCl₂ or CaCl₂ containing solution, in which Ni(NO₃)₂ may optionally added, according to a liquid /solid weight ratio of 2:1, followed by stirring and impregnating for 2 hrs, drying at 120°C, and then calcining at 550°C for 2 hrs. The resulting ZSM-5 prepared by the above procedure containing 4.9wt% of P₂O₅ and 0.9wt% of Al₂O₃ is marked as P · Al-Z zeolite, the one containing 5.0wt% of P₂O₅ and 1.4wt% of MgO is marked as P · Mg-Z zeolite, the one containing 4.9wt% P₂O₅ and 2.0wt% of CaO is marked as P · Ca-Z zeolite. The one containing 5.0wt% of P₂O₅, 1.4wt% of MgO and 1.2wt% of NiO is marked as P · Mg · Ni-Z.

Example 1~3

[0025] These examples demonstrate the preparation and the cracking performance of the catalyst of the present invention using clay as matrix, pseudo-boehmite as binder and single-component zeolite as active component.

[0026] Slurrying 13.5 Kg kaolin polyhydrate (a commercial product with a solid content of 73wt%) with 34.36 Kg de-cationized water, adding 13.5 Kg pseudo-boehmite (a commercial product with a solid content of 64wt%) and 1.17L hydrochloric acid (30wt%), stirring homogeneously, aging statically at 75°C for 1 hr, maintaining the pH value in the range of 2~4, lowering the temperature to 60°C, adding 15wt% of pre-prepared P · Al-Z or P · Mg-Z or P · Ca-Z zeolite respectively (anhydrous, based on the weight of catalyst), mixing homogeneously, spray drying, washing off the isolated sodium ions, and drying to obtain catalyst sample A or B or C.

[Comparative sample 1]

[0027] Using the phosphorus and rare earth metal containing high silica zeolite having a structure of pentasil having a silica/alumina mole ratio of 30, RE₂O₃ 2.0wt%, P₂O₅ 5.0wt%, a commercial product designated as ZRP, as active component instead of P · Al-Z or P · Mg-Z or P · Ca-Z zeolite to prepare comparative sample 1 according to the same procedure and composition used for the preparation of samples A,B and C.

[Comparative sample 2]

[0028] Using HZSM-5 zeolite, a commercial product having a silica/alumina mole ratio of < 55, as an active component instead of the P · Al-Z or P · Mg-Z or P · Ca-Z to prepare comparative sample 2 according to the procedure and composition used for the preparation of samples A, B and C.

[0029] Table 1 lists the chemical compositions of sample A,B and C. The evaluation results in a micro-reactor of sample A,B and C after hydrothermal treatment at 800 °C with 100% steam for 4 hrs. are presented in table 2. The reaction conditions used in micro-reactor for evaluating catalyst samples were: reaction temperature 520°C, catalyst/oil weight ratio 3.2, WHSV 16 h⁻¹, catalyst loading 5.0g, the properties of the feed as follows: distillation range 229~340°C, paraffinic hydrocarbon 45.5wt%, naphthenic hydrocarbon 35.7wt%, aromatic hydrocarbon 18.2wt%, colloid 0.6wt%.

[0030] Table 2 shows that the catalyst of the invention displays higher activity-stability; with the same zeolite content present in the catalyst and same hydrothermal treatment severity, the activity of the catalyst of the invention is 14 unit and 19 unit higher than that of comparative samples 1 and 2 respectively. The catalyst of the invention also exhibits higher C₂⁺ selectivity. The C₂⁺ yield of the catalyst of the invention is 2.5 times and 4 times that of comparative samples 1 and 2 respectively, and the C₂⁺/C₃⁺ ratio in the yields obtained by the catalyst of the invention is 3 times that of comparative sample 1 or 2.

Example 4

[0031] This example relates to the preparation and the cracking performance of the catalyst of the invention using clay as matrix, pseudo-boehmite as binder and dual-zeolites as active component.

[0032] Slurrying 15.3 Kg kaolin polyhydrate with 34.7Kg de-cationized water, adding 19.4Kg pseudo-boehmite and

EP 0 909 582 A1

1.65L hydrochloric acid, stirring homogeneously, aging statically at 75°C for 1 hr, maintaining the pH value in the range of 2-4, lowering the temperature to 60°C, adding 3.0Kg (anhydrous basis) P · Mg-Z zeolite, 0.8Kg (anhydrous basis) SRY zeolite (commercial name, stabilized Y type zeolite) and 5 Kg de-cationized water, homogenizing, spray drying, washing off the free sodium ions, and drying the resultant to obtain catalyst sample D.

5

10 Table 1

Catalyst sample	A	B	C	Comparative 1	Comparative 2
Composition, wt.%					
Kaolin clay	59.5	59.5	59.5	59.5	59.5
Al ₂ O ₃	25.5	25.5	25.5	25.5	25.5
Zeolite					
P · Al-Z	15.0				
P · Mg-Z		15.0			
P · Ca-Z			15.0		
ZRP				15.0	
HZSM-5					15.0

15

20 Table 2

Catalyst sample	A	B	C	Comparative 1	Comparative 2
Activity, wt%	63	62	63	49	44
Product yield, wt%					
Cracking gas	27.46	27.01	27.19	21.72	16.76
wherein, C ₂ =	3.30	3.16	3.18	1.35	0.82
C ₃ =	6.74	7.34	6.67	8.85	6.50
C ₄ =	3.97	4.61	4.04	6.79	5.63
C ₂ ~C ₄ , wt%	14.01	15.11	13.89	16.99	12.95
C ₂ =/C ₃ =	0.49	0.43	0.48	0.15	0.13

25

30

[Comparative sample 3]

35

[0033] Using the phosphorus and rare earth containing high silica zeolite having a structure of pentasil, known has ZRP (commercial name) as active component instead of P · Mg-Z zeolite used in example 4 to prepare comparative sample 3 according to the same procedure and composition used for the preparation of sample D.

40

[0034] Table 3 exhibits the composition of catalyst D and comparative sample 3. The evaluation results in micro-reactor for sample D and comparative sample 3 after hydrothermal treatment at 800°C with 100% steam for 4 hrs are indicated in table 4. The evaluation conditions were same to those used in example 1~3.

[0035] Table 4 shows that the C₂= yield and the C₂=/C₃= ratio in the yields obtained by the catalyst of the invention is 2.5 times and 3 times that of comparative sample 3 respectively.

45

50

Table 3

Catalyst sample	D	Comparative 3
Composition, wt.%		
Kaolin clay	53.0	53.0
Al ₂ O ₃	28.0	28.0
Zeolite, wt%		
P · Mg-Z	15.0	
ZRP		15.0
SRY	4.0	4.0

55

Table 4

Catalyst sample	D	Comparative 3
Activity, wt%	73	72
Cracking gas of, wt% wherein, $C_2 =$	33.4	25.39
$C_3 =$	3.29	1.32
$C_4 =$	7.61	8.99
$C_2 \sim C_4$, wt%	4.88	6.53
$C_2 = C_3$	15.78	16.84
	0.43	0.15

5

10

15 Example 5~7

[0036] These examples relate to the preparation and cracking performance in fixed fluidized bed (FFB) unit of the catalyst of the invention using clay as matrix, pseudo-boehmite as binder, and single component zeolite as active component.

[0037] Slurrying 3.39Kg kaolin polyhydrate with 11.45Kg de-cationized water, adding 2.10Kg pseudo-boehmite and 0.39 L hydrochloric acid, stirring homogeneously, aging statically at 75°C for 1 hr, maintaining the pH value in the range of 2~4, lowering the temperature to 60°C, adding 0.675Kg (anhydrous basis) P · Al-Z or P · Mg-Z or P · Ca-Z zeolite respectively, mixing homogeneously, spray drying, washing off the free sodium ions, and drying to obtain catalyst sample E or F or G.

25

[Comparative sample 4]

[0038] Using the phosphorus and rare earth containing high silica zeolite having a structure of pentasil, ZRP, as active component instead of the zeolite used in the catalyst of the invention to prepare the comparative sample 4 according to the procedure and composition used in examples 5~7.

[0039] The composition of the above catalyst samples are listed in table 5. Table 6 describes the results from FFB unit of the catalyst samples E,F and G after hydrothermal treatment at 800°C, 100% steam for 17 hrs. The comparative sample 4 was hydrothermal treated at 760°C, 100% steam for 10 hrs. The conditions of the evaluation were: reaction temperature 720°C, catalyst/oil weight ratio 10, WHSV 10hr⁻¹, water injection 80 wt%, catalyst load 180g, the distillation range of the feed for FFB test is 346~546°C, UOP K value of the feed 12.4, CCR (Conradson Carbon Residue) 0.15wt%, density (20°C) 0.8730g/cm³.

[0040] The data from table 6 indicate that $C_2 =$ yield of the catalyst of the invention is increased by 3~5wt%.

Table 5

Catalyst sample	E	F	G	Comparative 4
Composition, wt%				
Kaolin clay	55	55	55	55
Al_2O_3	30	30	30	30
Zeolite				
P · Al-Z	15			
P · Mg-Z		15		
P · Ca-Z			15	
ZRP				15

40

45

50

Table 6

Catalyst sample	E	F	G	Comparative 4
Product yield, wt%				
Cracking gas wherein, $C_2 =$	74.30 22.70	68.33 21.00	69.27 21.38	63.88 18.35

EP 0 909 582 A1

Table 6 (continued)

Catalyst sample	E	F	G	Comparative 4
$C_3^=$	20.88	18.88	18.75	20.97
$C_4^=$	8.56	7.81	8.18	10.42
Gasoline (C_5 ~221°C)	12.07	16.05	14.68	13.80
LCO (221~330°C)	2.66	4.17	4.25	8.77
Heavy Oil (> 330°C)	1.04	1.42	1.97	8.52
Coke	9.93	10.03	9.83	5.03
Conversion, wt%	96.30	94.41	93.78	82.71
$C_2^= + C_3^= + C_4^=$, wt%	52.14	47.61	48.31	49.74
$C_2^= / C_3^=$	1.09	1.11	1.14	0.87

15 Examples 8~10

[0041] These examples describe the preparation and the cracking performance in FFB unit of the catalyst of the invention using clay as matrix and amorphous silica alumina as binder.

[0042] 12Kg water glass (SiO_2 content of 243g/l, density 1.246) was diluted by 43Kg de-cationized water, mixing homogeneously, adding 1.9Kg kaolin polyhydrate and 0.75Kg (anhydrous basis) P Al-Z zeolite, stirring homogeneously, adding slowly to it 3Kg aluminum sulfate solution (alumina content of 93.5 g/l, density 1.287) and 5.6Kg de-cationized water. The pH value of the sample was controlled at 10~11 and aging dynamically for 30 min, adding slowly to it 2.6Kg aluminum sulfate solution, controlling the pH value in the range of 4~5, then aging dynamically once more for 20 min. After filtering the above mixture, slurring the resultant with 15 Kg de-cationized water, spray drying, washing and drying finally to obtain the catalyst sample H.

[0043] Using P · Mg-Z zeolite or P · Ca-Z zeolite instead of P · Al-Z zeolite to obtain the catalyst sample I or J.

[Comparative sample 5]

[0044] Using phosphorus and rare earth metal containing high silica zeolite having a structure of pentasil, ZRP, as active component instead of the zeolite used in the catalyst of the invention to prepare the comparative sample 5 according to the procedure and composition used in examples 8~10.

[0045] Table 7 lists the composition of the above catalyst samples. The evaluation results of the above catalysts after hydrothermal treatment at 800°C, 100% steam for 17hrs are illustrated in table 8, the evaluation conditions are same to that of example 5-7 except that the reaction temperature was 700°C.

[0046] The data in table 8 show that the yields of cracking gas, $C_2^=$, and $C_2^= \sim C_4^=$ by the catalyst of the invention are 2~3wt%, 2wt% and 4wt% higher respectively than those of comparative sample 5.

Table 7

Catalyst sample	H	I	J	Comparative 5
Composition, wt%				
Kaolin clay	28	28	28	28
$SiO_2 \cdot Al_2O_3$	57	57	57	57
Zeolite				
P · Al-Z	15			
P · Mg-Z		15		
P · Ca-Z			15	
ZRP				15

Table 8

Catalyst sample	H	I	J	Comparative 5
Product yield, wt%				
Cracking gas wherein, $C_2^=$	69.32 20.41	69.70 20.77	68.61 19.81	66.37 18.31

Table 8 (continued)

Catalyst sample	H	I	J	Comparative 5
$C_3^=$	22.52	22.47	22.72	21.77
$C_4^=$	10.61	10.69	10.53	9.32
Gasoline (C_5 ~221°C)	15.05	15.22	17.84	14.97
LCO (221~330°C)	5.16	5.33	3.73	5.87
Heavy Oil (> 330°C)	4.10	3.65	2.64	4.89
Coke	6.37	6.10	7.18	7.90
Conversion, wt%	90.74	91.02	93.63	89.24
$C_2^= + C_3^= + C_4^=$, wt%	53.54	53.93	53.06	49.40

15 Example 11~12

[0047] These examples illustrate the preparation and cracking performance of the catalyst of the present invention using clay as matrix, pseudo-boehmite and aluminum sol as binder, and double-components of zeolite as active component.

[0048] Slunyng 3.26Kg kaolin polyhydrate with 10.7Kg de-cationized water, adding 1.82Kg pseudo-boehmite and 0.337L hydrochloric acid, stirring homogeneously, aging statically at 75°C for 1 hr, maintaining the pH value in the range of 2~4, lowing the temperature to 60°C, adding 0.642Kg aluminum sol (a commercial product with Al_2O_3 content of 0.2164wt%), stirring homogeneously, adding 0.675Kg (anhydrous basis) P · Mg-Z zeolite and 0.135Kg (anhydrous basis) SRY zeolite and 3.68Kg de-cationized water, homogenizing, spray drying washing off the isolated sodium ions, and drying to obtain the catalyst sample K.

[0049] Using P · Mg · Ni-Z zeolite instead of P · Mg -Z zeolite to prepare catalyst sample L.

[comparative sample 6]

[0050] Using the phosphorus and rare earth containing high silica zeolite having a structure of pentasil, ZRP, as active component instead of the zeolite used in the catalyst of the invention to prepare the comparative sample 5 according to the procedure and composition used in example 11~12.

[0051] Table 9 lists the composition of the above catalyst samples. The evaluation results from FFB Unit of the above catalyst samples after hydrothermal treatment at 800°C, 100% steam for 17 hrs are described in table 10, the evaluation conditions are same to that of example 5-7 except that the reaction temperature was 680°C.

[0052] The data in table 10 show that the yields of $C_2^=$ and $C_2^= - C_4^=$ by the catalyst of the invention are 2~5wt% and 1.5~4.5wt% higher respectively than those of comparative sample 6.

Table 9

Catalyst sample	K	L	Comparative 6
Composition, wt%			
Kaolin clay	53	53	53
Al_2O_3	29	29	29
Zeolite			
P · Mg-Z	15		
P · Mg · Ni-Z		15	
ZRP			15
SRY	3	3	3

Table 10

Catalyst sample	K	L	Comparative 6
Product yield, wt%			
Cracking gas wherein, $C_2^=$	73.17 19.20	70.48 22.26	69.06 17.55

Table 10 (continued)

Catalyst sample	K	L	Comparative 6
$C_3^=$	27.83	22.66	24.88
$C_4^=$	11.30	10.37	11.31
Gasoline ($C_5 \sim 221^\circ C$)	10.07	14.36	10.09
LCO ($221 \sim 330^\circ C$)	4.52	3.48	3.93
Heavy Oil ($> 330^\circ C$)	3.23	3.40	4.07
Coke	9.01	8.28	12.85
Conversion, wt%	92.25	93.12	92.00
$C_2^= + C_3^= + C_4^=$, wt%	58.33	55.29	53.74

Example 13

[0053] This example illustrates the preparation and cracking performance of the catalyst of the present invention using clay as matrix, pseudo-boehmite and aluminum sol as binder and double component of zeolite as active component.

[0054] The catalyst sample 13 is prepared in a pilot plant of catalyst preparation. Slurrying 132.4Kg kaolin polyhydrate with 428Kg de-cationized water, adding 72.8Kg pseudo-boehmite and 13.48L hydrochloric acid, stirring homogeneously, aging statically at $75^\circ C$ for 1hr, maintaining the pH value in the range of 2~4, lowering temperature to $60^\circ C$, adding 24.96Kg aluminum sol, stirring homogeneously, adding 36Kg (anhydrous basis) P · Mg-Z zeolite and 63Kg (anhydrous basis) SRY and 147Kg de-cationized water, homogenizing, spray drying, washing off the free sodium ions and drying to obtain the catalyst sample M.

[0055] Table 11 lists the composition of catalyst sample M. The evaluation results from pilot plant riser of catalytic pyrolysis cracking of sample M after hydrothermal treatment at $790^\circ C$, 100% steam for 27 hrs in a pilot plant hydrothermal treating are described in table 12. The catalyst inventory of the pilot plant riser is 55Kg. The properties of the feedstock used are as follows: density ($20^\circ C$) 0.8826g/cm^3 , carbon residue 2.9wt%, freezing point $46^\circ C$, saturate hydrocarbon 59.8wt%, aromatic hydrocarbon 26.4wt%, colloid 13.2wt%, asphaltene 0.6wt%.

Table 11

Catalyst sample	M
Composition, wt%	
Kaolin clay	51.5
Al_2O_3	25
Zeolite	
P · Mg-Z	20
SRY	3.5

Table 12

Catalyst sample	M
Operation condition	
reaction temp., $^\circ C$	660
reaction pres. (gauge), Kg/cm^2	0.07
feeding rate, Kg/hr	2.2
water injection (based on total feed), wt%	80
catalyst/oil ratio	37
residual time, sec.	1.4
regeneration temp., $^\circ C$	720
feed preheat temp., $^\circ C$	333
Product yields, wt	
cracking gas	61.53
wherein dry gas	40.34

Table 12 (continued)

Catalyst sample	M
liquefied gas	21.19
liquid product	26.92
coke	10.30
loss	1.25
total	100
Gas product yields, wt	
CH ₄	12.96
C ₂ H ₄	21.86
C ₃ H ₆	15.04
C ₄ H ₈	5.70
C ₂ =+ C ₃ =+ C ₄ =	42.60

Claims

1. A catalyst composition which comprises 10 to 70 wt% (based on the weight of the catalyst) of clay, 5 to 85 wt% of inorganic oxides and 1 to 50 wt% of zeolite, wherein said zeolite comprises 0 to 25 wt% Y type zeolite and 75 to 100 wt% of phosphorus and aluminum or phosphorus and magnesium or phosphorus and calcium containing high silica zeolite having a structure of pentasil, said high silica zeolite is ZSM-5, ZSM-8 or ZSM-11 type zeolite containing 2 to 8 wt% (based on the weight of the zeolite) of phosphorus and 0.3 to 3 wt% of aluminum or magnesium or calcium (calculated as the oxides), having a silica/alumina mole ratio of 15 to 60.
2. A catalyst composition according to claim 1, wherein said clay is selected from kaolin or kaolin polyhydrate clay.
3. A catalyst composition according to claim 1 or 2, wherein said inorganic oxides are selected from amorphous silica-alumina, alumina or silica.
4. A catalyst composition according to any preceding claim, wherein said Y type zeolite is selected from REY (rare earth metal ion exchanged Y) zeolite with a content of rare earth metal not less than 14 wt% (calculated as RE₂O₃) or a stabilized high silica Y type zeolite with relatively high silica/alumina mole ratio prepared by chemical and/or physical treatment.
5. A catalyst composition according to any preceding claim, wherein said phosphorus and aluminum or phosphorus and magnesium or phosphorus and calcium containing high silica zeolite having a structure of pentasil may also contain 0.3 to 3 wt% (based on the weight of the zeolite) of nickel (calculated as the oxide).
6. A method for the preparing of the catalyst according to claim 1, characterized by the steps of mixing the precursor of the inorganic oxides with clay to obtain a slurry with a solid content of 10 to 50 wt%, adjusting with an inorganic acid and maintaining the pH value of the slurry at 2 to 4, after aging statically at 20 to 80°C for 0 to 2 hrs, adding zeolite, homogenizing, spray drying, washing and drying.
7. A method according to claim 6, wherein the precursor of the inorganic oxides is selected from the group consisting of aluminum sol, pseudoboehmite, silica sol and the mixtures thereof, and silica alumina sol or gel.
8. A method according to claim 6 or 7, wherein said zeolite in the catalyst is a phosphorus and aluminum or phosphorus and magnesium or phosphorus and calcium containing high silica zeolite having a structure of pentasil or a mixture of said high silica zeolite and Y type zeolite.
9. A method according to claim 8, wherein said pentasil high silica zeolite is selected from the group consisting of ZSM-5, ZSM-8 and ZSM-11 type zeolites containing 2 to 8 wt% of phosphorus (based on the weight of zeolite) and 0.3 to 3 wt% of aluminum or magnesium or calcium (calculated as the oxides).
10. A method according to claim 8 or 9, wherein said pentasil high silica zeolite may also contain 0.3 to 3 wt% (based

on the weight of the zeolite) or nickel (calculated as the oxide).

- 5 11. A method according to claim 8 or 9, characterized in that the preparation of said phosphorus and aluminum or phosphorus and magnesium or phosphorus and calcium containing pentasil high silica zeolite comprises the steps of: adding ZSM-5 or ZSM-8 or ZSM-11 type zeolite into an aqueous solution containing phosphorus and aluminum or phosphorus and magnesium or phosphorus and calcium compounds with a water/solid ratio of 1 to 3:1, mixing homogeneously, impregnating for 0.5 to 4 hrs, drying at 100 to 120°C, and calcining at 450 to 650°C for 1 to 4 hrs.
- 10 12. A method according to claim 11, wherein said phosphorus compound containing aqueous solution is phosphoric acid aqueous solution, and said aluminum or magnesium or calcium compound containing aqueous solutions are selected from aqueous solutions of their nitrates, hydrochlorides or sulfates.
- 15 13. Use of a catalyst composition according to any of claims 1 to 5 in the catalytic pyrolysis of hydrocarbons to produce light olefins, especially ethylene, propylene and butylene.

20

25

30

35

40

45

50

55



DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)						
D,A	US 5 380 690 A (MENG ZHOU ET AL) 10 January 1995 * claims 1-9 * * column 2, line 53 - column 3, line 55 * ---	1-4,6-9, 13	B01J29/06 C10G11/05 B01J29/40 B01J29/46						
A	CHEMICAL ABSTRACTS, vol. 114, no. 16, 22 April 1991 Columbus, Ohio, US; abstract no. 145779, LI, D., TAO, L., ZHANG, Y., WANG H., HAEN J. AND ZHENG L.: "Effect of phosphorus and magnesium on acidity, activity and olefin selectivity of H-ZSM 5 zeolite" XP002090576 * abstract * & SHIYOU HUAGONG, vol. 19, no. 7, 1990, pages 449-454, ---	1-4,13							
A	EP 0 541 191 A (GRACE W R & CO) 12 May 1993 * claims 1-3,5-9,14-17 * ---	1-4,13							
A	EP 0 727 404 A (CHINA PETRO CHEMICAL CORP ;RES INST OF PETROLEUM PROCESSI (CN)) 21 August 1996 * claims 1,6-11,18,19 * * page 3, line 20 - line 44 * * example 3 * ---	1-4,13	B01J C10G						
A	EP 0 305 720 A (RES INST OF PETROLEUM PROCESSI) 8 March 1989 * claims 1-5 * * page 2, line 54 - page 3, line 22 * * tables 1,4,6,7 * ---	1-3,13 -/-							
<p>The present search report has been drawn up for all claims</p> <table border="1"> <tr> <td>Place of search</td> <td>Date of completion of the search</td> <td>Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>26 January 1999</td> <td>Zuurdeeg, B</td> </tr> </table> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>				Place of search	Date of completion of the search	Examiner	THE HAGUE	26 January 1999	Zuurdeeg, B
Place of search	Date of completion of the search	Examiner							
THE HAGUE	26 January 1999	Zuurdeeg, B							



European Patent Office

EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 355 928 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 28 February 1990 * claims 1-12,14 * -----	1-3,13	
TECHNICAL FIELDS SEARCHED (Int.Cl.6)			
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	26 January 1999	Zuurdeeg, B	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 98 30 8445

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

26-01-1999

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 5380690	A	10-01-1995		CN 1093101 A	05-10-1994
				NL 9301333 A	17-10-1994
EP 0541191	A	12-05-1993		US 5302567 A	12-04-1994
				DE 69217610 D	03-04-1997
				DE 69217610 T	17-07-1997
				ES 2097863 T	16-04-1997
				JP 5214347 A	24-08-1993
				US 5382351 A	17-01-1995
EP 0727404	A	21-08-1996		CN 1102431 A	10-05-1995
				FI 961881 A	03-07-1996
				JP 9504817 T	13-05-1997
				CA 2175656 A	11-05-1995
				WO 9512562 A	11-05-1995
				NL 9400709 A	01-06-1995
				US 5670037 A	23-09-1997
EP 0305720	A	08-03-1989		CN 1031834 A	22-03-1989
				DE 3889040 D	19-05-1994
				DE 3889040 T	03-11-1994
				JP 1110635 A	27-04-1989
				JP 1937910 C	09-06-1995
				JP 6067857 B	31-08-1994
				US 4980053 A	25-12-1990
EP 355928	A	28-02-1990		AU 616791 B	07-11-1991
				AU 4021289 A	01-03-1990
				CA 1333576 A	20-12-1994
				CN 1040609 A, B	21-03-1990
				GR 3005150 T	24-05-1993
				JP 2113090 A	25-04-1990
				JP 2707140 B	28-01-1998
				US 4976847 A	11-12-1990